MAPbI₃ Single Crystals Free from Hole-Trapping Centers for Enhanced Photodetectivity

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Supporting Information

ABSTRACT: Perovskite single crystals (PSCs) are considered the next breakthrough in optoelectronics research due to their free-grain boundary and much lower density of trap states compared to those of their polycrystalline counterparts. However, the inevitable formation of triiodide-based intrinsic defects during high-temperature crystal growth is one of the major challenges impeding the further development of optoelectronic devices based on PSCs. Here, we not only identified the existence of these triiodide ions as hole-trapping centers and their tremendous negative impact on the performance of PSCs, but more importantly, we used a reduction treatment to prevent their formation during crystal growth. The removal of such defect centers resulted in much higher charge carrier mobility and longer carrier lifetime than the untreated counterparts, leading to enhanced photo-detection properties. The I₃⁻-free MAPbI₃ single crystal (MSC) devices consistently generated a more than 100 times higher photocurrent than that generated by I₃⁻-rich devices under the same light intensity.

Over the past decade, hybrid organic–inorganic lead halide perovskites have become the fastest advancement track in solar technology, marking a new era in developed and high-performing optoelectronic devices.^{1–3} In particular, hybrid perovskite single crystals (PSCs) stand out for their longer diffusion length, higher carrier mobility, free-grain boundary, and longer charge carrier lifetime compared to their polycrystalline counterparts.^{4–6} These advantages are mainly a result of their lower trap density. However, the photodetectors and solar cells made using polycrystalline films, regardless of their grain boundary defects, are often known to outperform those made of bulk single crystals.^{5–7} This difference could be attributed to the hydration of single-crystal facets along with inevitable surface and bulk contamination due to crystal growth, which can severely impact optoelectronic performance.^{8–10} In this regime, significant efforts are being made to attain a neat subsurface structure and composition to further enhance the quality of bulk single crystals.^{11–15} In this work, we uncovered the existence of intrinsic defects in the form of triiodide ions (I₃⁻) within the structure of methylammonium lead iodide (MAPbI₃) single crystals (MSCs). We find that during the synthesis process,

either by using an inverse temperature⁵ or temperature lowering method,¹⁶ the existing free iodide ions (I⁻) tend to be oxidized to I₃⁻ ions, as shown in eqs 1 and 2, which act as hole-trapping centers that negatively impact the charge carrier mobility and carrier recombination dynamics, deteriorating the optoelectronic performance of MSCs. To eliminate these intrinsic monovalent defects, we added hypophosphorous acid (H₃PO₂) to prevent the formation of I₃⁻ ions by suppressing the oxidation of iodine, as described in eq 3. It is worth pointing out that the addition of H₃PO₂ would make the mother solution of the PSC efficiently recyclable, which would further decrease the industrial production cost.

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Figure 1. Evidence of the I_3^- formation during the growth of PSCs. (a) Color guide of MAI (left) and H_3PO_2 -containing MAI (right) dissolved in GBL and heated under different temperatures. (b) Corresponding UV–Vis absorption spectra of the MAI solutions with and without H_3PO_2 at different temperatures (20, 60, 75, 90, and 100 °C).¹⁷

Figure 2. (a) I_3^-/I^- ratio in I_3^- -free (red) and I_3^- -rich (grown at 60, 75, 90, and 100 °C) MSCs as obtained by mass spectrometry. Insets are the precursors in which the I_3^- -rich single crystals were grown. (b) Hall mobility of the I_3^- -free and I_3^- -rich MSCs. (c) TRPL of I_3^- -free grown at 100 °C (red) and I_3^- -rich (grown at 60, 75, 90, and 100 °C) single crystals with a τ_{av} of 3.13 ± 0.03, 1.79 ± 0.02, 1.65 ± 0.01, 1.03 ± 0.01 and 0.94 ± 0.01 ns, respectively. (d) Steady-state photoluminescence of the five studied single crystals. (e) Liquid-state ¹H NMR of the I_3^- -free and I_3^- -rich single crystals dissolved in deuterated DMSO. The ¹H NMR spectrum of pure H_3PO_2 is shown at the bottom.

To highlight the spontaneous formation of I_3^- ions, MAI is added to gamma-butyrolactone (GBL), forming a transparent solution that turns yellow at room temperature (ca. 20 °C). However, as the temperature increases (60, 75, 90, and 100

°C), the solution exhibits a progressively darker color until it turns reddish brown at 100 °C, as shown in Figure 1a (left). This gradual color change is attributed to the formation of I_3^- ions, which correlates well with the augmentation observed in

Figure 3. (a) Projected density of states (PDOS) and electronic charge density of the VBM and CBM for the MAPbI₃ supercell. (b) PDOS and charge-transition level of the MAPbI₃ supercell with negatively charged iodine (I₃⁻). The inset shows the electronic charge density of the I₃⁻ defect state. (c) Schematic energetic diagram and crystal lattice of I₃⁻-free and (d) I₃⁻-rich MSCs.

the two characteristic UV–Vis absorption peaks of I₃⁻ at 294 and 365 nm (Figure 1b).¹⁰ It should be noted that when the heating process is carried out in a glovebox (in the absence of oxygen), the amount of I₃⁻ ions formed dramatically decreases, as indicated by the light yellow color (Figure S1), highlighting the role of oxygen in stimulating the oxidation reaction to form triiodide. Accordingly, extra precautions must be taken to avoid/reduce the formation of I₃⁻ ions. In this context, growing them under vacuum or a nitrogen flow might be a good choice. However, this is a relatively costly option. Instead, we use H₃PO₂ as a powerful reducing agent to halt the oxidation of I⁻ ions into I₃⁻. In fact, adding 1% of H₃PO₂ is enough to abolish the formation of I₃⁻ ions, as evidenced by the absence of the two peaks at 294 and 365 nm (Figure 1b) and by the unaltered transparency of the MAI solution, even at elevated temperatures, as demonstrated in Figure 1a.

For further investigations, we grew four MSCs under different temperatures (60, 75, 90, and 100 °C), while a fifth single crystal was grown at 100 °C using an H₃PO₂-containing precursor to form I₃⁻-free MSCs. We then quantified the amount of I₃⁻ ions in the fabricated single crystals using mass spectrometry (negative mode). The corresponding mass spectra of the five single crystals (from 100 to 700 *m/z*) are depicted in Figure S2. As expected, the characteristic peak of I₃⁻ at 380 *m/z* exhibits a much higher intensity for the MSCs grown at higher temperatures in pristine MAPbI₃ solutions. In contrast, for the MSCs grown at 100 °C in an H₃PO₂-containing MAPbI₃ precursor solution, no peaks were detected at 380 *m/z*, providing a clear indication of the absence of I₃⁻ ions. The ratio of the formed I₃⁻ to I⁻ in the five crystals is plotted in Figure 2a, and the results are in excellent agreement with the steady-state absorption and color change shown in Figure 1.

To probe the defect concentration in our MSCs, we measured their corresponding Hall mobility and free carrier concentration.¹¹ Notably, the aforementioned increase of the I₃⁻ ions led to a significant deterioration in the Hall mobility of

the MSCs, as illustrated in Figure 2b. The remarkably higher Hall mobility for I₃⁻-free MSCs is clearly indicative of the direct proportionality between the I₃⁻ content and the density of the intrinsic defects within the electronic structure of the PSCs. Moreover, the carrier concentration also increased by several orders of magnitude in the absence of I₃⁻, ca. 10⁹ for I₃⁻-rich to ca. 10¹⁴ cm⁻³ for I₃⁻-free MSCs. Such an increase in the charge carrier mobility and the sharp decrease in I₃⁻ concentration are accompanied by a corresponding increase in the charge carrier lifetime, as measured by time-resolved photoluminescence (TRPL), providing another strong piece of experimental evidence for the high-quality I₃⁻-free PSCs. Figure 2c shows that the average carrier lifetime (τ_{av}) in I₃⁻-free MSCs (3.13 ns) is three times longer than that of I₃⁻-rich single crystals prepared at 100 °C (0.94 ns). The enhancement in the carrier mobility and charge carrier lifetime underlines the finer quality of both bulk and surface characteristics of the I₃⁻-free MSC in comparison with those of I₃⁻-rich MSCs. The corresponding photoluminescence and UV–Vis absorption spectra of the studied PSCs are shown in Figures 2d and S3.

Thus far, the effect of H₃PO₂ on the formation of I₃⁻ has been emphasized. To understand the chemical interaction of H₃PO₂ with our MSCs, we performed extensive liquid-state ¹H NMR spectroscopy. The corresponding spectra of either I₃⁻-rich or I₃⁻-free MSCs (Figure 2e) reveal the absence of the PH doublet peaks at 7.47 and 6.56 ppm, characteristic of H₃PO₂, indicating no interaction with the single crystal. The other two peaks at 7.50 and 2.38 ppm are assigned to the hydrogen in the amino and methyl groups, respectively. In conclusion, unlike their polycrystalline counterparts, which tend to form PbHPO₃ nanoparticles in the presence of H₃PO₂,⁹ our MSCs do not exhibit any chemical interaction upon H₃PO₂ addition. In this regime, it is worth mentioning that, owing to the high density of defect states in polycrystalline films, triiodide ions may act differently and passivate the surface defects and control the phase change, subsequently enhancing the device performance.¹⁸

Figure 4. (a) Semilog scale I – V characteristics of I_3^- -rich (black) and I_3^- -free (blue) MSC photodetectors in the dark (open circles) and under illumination (solid circles) at a wavelength of 447 nm with an intensity of 3.3 mW cm^{-2} . All devices were kept under a bias voltage of $\pm 1 \text{ V}$. Insets: Photographs of single I_3^- -free (top-left) and I_3^- -rich (bottom-right) MSC photodetector cells. (b) Semilog scale I – V characteristics of a I_3^- -free MSC photodetector under 447 nm light illumination at different intensities. Inset: Photograph of an array of two-terminal, parallel-type I_3^- -free MSC devices. (c) (Blue) Temporal photoresponse of I_3^- -free MSC photodetectors at 1 V under alternating darkness and 447 nm light illumination with an intensity of 3.3 mW cm^{-2} . (Red) Photostability of the single-crystal devices at a wavelength of 447 nm with an intensity of 3.3 mW cm^{-2} . (d) Photocurrent (orange), responsivity (black), detectivity (blue), and EQE (red) of the single-crystal photodetector at -1 V as a function of light intensity at a wavelength of 447 nm. (e) Comparison between the photocurrents of I_3^- -rich (solid cylinders) and I_3^- -free (transparent cylinders) MSC devices, measured at wavelengths of 253 (light violet), 300 (violet), 447 (blue), 532 (green), and 660 nm (red). The values are obtained at light intensities of 4.9 mW cm^{-2} for 253 and 300 nm, 3.3 mW cm^{-2} for 447 nm, 3.65 mW cm^{-2} for 532 nm, and 4.7 mW cm^{-2} for 660 nm. (f) Semilog scale I – V characteristics of an I_3^- -free MSC photodetector illuminated by the display of a cell phone at low (blue) and high brightness (green) and by the flashlight (orange) of the same phone. Inset: Schematic architecture of an array of MSC photodetectors.

To elucidate the negative impact of the triiodide ions on the electronic and optical properties of MSCs, we inspected the charge-trapping process of interstitial iodine (I_i) in MAPbI_3 based on the tetragonal-phase MAPbI_3 supercell model using density functional theory (DFT) calculations. As shown in Figure 3a,b, the perfect MAPbI_3 crystal shows delocalized electronic densities for both the conduction band minimum (CBM) and valence band maximum (VBM). However, once the negatively charged interstitial iodine (I_i^-) is present, the defect iodide atoms form a bridged dimer geometry (i.e., two iodine atoms bind to two lead atoms in bridging coordination), and the I_i^- state behaves as a hole-trapping center with a transition level of 0.22 eV above the VBM with a highly localized charge density (green area). Such hole-trapping centers are expected to capture photogenerated charge carriers and act as nonradiative centers, leading to degradation in the optoelectronic performance of the single crystals (Figure 3c,d).^{19,20} It should be noted that De Angelis and co-workers have conducted high-level DFT calculations, and the results

confirm that I_i^- generates hole-trapping centers in the bandgap.²⁰

To take our work one step further, we investigated the negative effect of the I_i^- -based intrinsic defects on the optoelectronic performance of our single crystals. Hence, we used e-beam evaporation to deposit gold electrodes (ca. 100 nm thick) on the (100) facet of bulk I_3^- -rich (grown at 100°C) and I_3^- -free MSCs (grown at 100°C), forming different arrays of two-terminal, parallel-type planar photodetectors (see insets of Figure 4a,b,f). The typical X-ray diffraction (XRD) pattern of the top facet of fabricated bulk MSCs is displayed in Figure S4. The detailed photodetector fabrication procedure is also explained in the Experimental Details section. It is worth mentioning that this is not the best photodetector architecture. However, we intentionally selected such a simple device structure with a rather large channel length of $70 \mu\text{m}$ to clearly distinguish the performance of I_3^- -free MSC over its I_3^- -rich counterpart.

To examine the photodetectivity of our fabricated MSC devices in the visible-spectral region, we investigated their

photoresponse characteristics under five distinct excitation wavelengths (253, 300, 447, 532, and 660 nm). All measurements were conducted under ambient conditions using various light intensities. Both MSC photodetectors demonstrated a broad-band UV–Vis spectral photoresponse; however, the I_3^- -free devices consistently generated a more than 100 times higher photocurrent than the I_3^- -rich devices under the same light intensity. This boost in photodetection performance is attributed to the increase in the carrier concentration along with the reduction in hole-trapping centers. The corresponding photodetection characteristics of I_3^- -rich and I_3^- -free MSC devices are presented in Figures 4 and S5–S10. A comparison between the current–voltage (I – V) characteristics of I_3^- -free (blue) and I_3^- -rich (black) MSC photodetectors illuminated with the same light intensity (3.3 mW cm^{-2}) at a representative wavelength of 447 nm is shown in Figure 4a. Figure 4b illustrates the gradual increase in the generated photocurrent of I_3^- -free MAPbI₃ devices as a function of light intensity at 447 nm. Remarkably, a light intensity as low as $5 \mu\text{W cm}^{-2}$ was enough for the photocurrent of the I_3^- -free devices to increase from 1 to 40 nA. In contrast, Figure S6a shows that, at the same low light intensity, the photocurrent of the I_3^- -rich MSC photodetectors only increased from 0.2 to 1.2 nA, which is attributed to the I_3^- -based trap centers hindering the flow rate of the carriers. The prominent enhancement in the photoresponse of I_3^- -free MSCs, with respect to their I_3^- -rich counterparts, correlates well with the aforementioned increase in their carrier concentration and carrier mobility (see Figure 2b). Interestingly, the generated photocurrent of our I_3^- -free MSC photodetectors is in agreement with previous reports,^{21,22} although the channel length of our parallel planar-type devices is significantly larger ($70 \mu\text{m}$) relative to the much shorter channels in other reports.^{22,23} Additionally, the photocurrent of our single-crystal photodetectors is as high as that generated by epitaxially grown MAPbI₃,²⁴ which is typically known to outperform single crystals. For an overall comparison between the broad-band photoresponse of our I_3^- -rich and I_3^- -free MSCs, the generated photocurrent at each of the excitation wavelengths is shown in Figure 4e. The depicted photocurrents were all obtained at the same light intensity (ca. 4 mW cm^{-2}). Figure 4c demonstrates the reliable photoswitching characteristics of the I_3^- -free devices at a bias voltage of 1 V under alternating light (447 nm) and dark conditions. Both I_3^- -free and I_3^- -rich MSC photodetectors maintained good photostability, with no degradation, for more than 8000 s under the same excitation of 447 nm light, as shown in Figures 4c and S6f.

Furthermore, to underscore the high quality of the I_3^- -free MAPbI₃, we evaluated its irradiance-power-dependent characteristics in comparison with those of I_3^- -rich MSCs. Considering the large effective illuminated area of our devices, we calculated their responsivity (R), specific detectivity (D^*), and external quantum efficiency (EQE) under excitation at five representative wavelengths with different light intensities (Figures 4d and S5–S10). Analogous to previous reports, we performed the calculations supposing that the dark current is dominated by the shot noise (see Table S1).^{25–27} Figures 4d and S6 display the R , D^* , and EQE for I_3^- -free and I_3^- -rich MAPbI₃ devices under an incident light of 447 nm at an intensity of 3.3 mW cm^{-2} at a bias voltage of -1 V . At the same light intensity, the removal of the I_3^- -based intrinsic defects amplified the R by 30 times and the D^* by 12 times,

while the EQE was strikingly enhanced by ca. 27 times and increased from 64% for I_3^- -rich to 1723% for I_3^- -free MSC photodetectors. Furthermore, our devices not only revealed an enhanced photoresponse when excited with focused light sources (i.e., laser beams) but they also demonstrated a high sensitivity for unfocused white light illumination coming from LCD display screens. Figure 4f shows how the I_3^- -free MSC photodetector responded to illumination from a regular cell phone display and its flashlight.

In summary, we pinpointed the existence of hole-trapping centers within the structure of MSCs in the form of I_3^- ions, which are spontaneously formed during typical high-temperature growth methods. Here, we successfully abolished the formation of such intrinsic defects, leading to a boost in the carrier mobility, carrier lifetime, and optoelectronic device performance of MSCs. We have shown that I_3^- -free MSC photodetectors clearly outperform their I_3^- -rich counterparts. The broad-band photodetectors based on I_3^- -free MSCs exhibited an enhancement of more than 2 orders of magnitude in the generated photocurrent compared to the I_3^- -rich MSCs. Our findings underline the significance of developing new synthesis protocols for hybrid metal halide perovskite crystals to realize and unlock their full potential for optoelectronic applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsenerylett.9b01956](https://doi.org/10.1021/acsenerylett.9b01956).

Additional experimental results, including photographs of MAI solutions, mass spectroscopy, UV–Vis absorbance, X-ray diffraction patterns, and photodetection performance of I_3^- -free and I_3^- -rich MSCs under different excitation wavelengths (PDF)

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Notes

The authors declare no competing financial interest.

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